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Comparison between joining technologies for polymeric films

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Abstract

The packaging industry makes extensive use of thermoplastic polymers in film format that can have a thickness of less than 100 microns. Joining such thin films requires a tight control of several process parameters and of material homogeneity. Among the available technologies, heat sealing is widely applied along with solvent based gluing that is the more traditional technique.
In this paper, welds of thin polymeric films have been produced by means of a solid-state Laser source and the solvent based technique with the aim to compare their performances. Thin films specimens were cut from commercial rolls used in labelling applications or prepared from purposely-designed polymer blends by compression between the heated plates of a laboratory press. Blends prepared in laboratory using poly(lactic acid) or poly(lactide) blended with different percentage of an impact modifier were designed to test the sealing properties under laser welding irradiation respect to solvent bonding.
The solid-state laser source allows a short process time without direct contact between tool and part and thus without contamination of the film. Solvent gluing tests, by dispersing a controlled amount of solvent with a micro syringe by hand, were carried out. The material was characterized by means of differential scanning calorimetry, DSC. Changes along the welded lines by laser radiation and solvent gluing were characterized by micro FTIR and micro Raman techniques. An Instron 5966 testing machine, in the tensile mode, was used for measuring the strengths of the bonded films.

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Keywords: Joining; Welding; Polymer; Laser.

1. Introduction

The concern about the intensive exploitation of non-renewable fossil resources that are expected to be strongly depleted in a few decades (at least as far as crude oil is concerned) combined with the ever growing concern about the effects of the increasing amount of carbon dioxide released into the atmosphere by all sort of human activities are stimulating the increasing interest on bio-based plastics. According to the European Bioplastic Federation, bio-based plastics are polymer materials obtained from biomass and they can be biodegradable or not. The forecast of market expansion for bioplastics is still low, but the trend is for a fast growth.

Among the different bioplastics, poly(lactic acid) or poly(lactide), PLA in short, is the most promising materials for several reasons. It is a well-known polymer, already prepared and studied by W. Carothers back in 1930’s that can be prepared by polymerization of lactic acid.

In Nature, two enantiomers of lactic acid do exist, S- and R-lactic acid (or, according to and older nomenclature, L- and D-lactic acid), yielding PLLA and PDLA homopolymers. Some properties

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of PLA, especially crystallinity and crystallization rate, can be easily controlled by the ratio between L- and D- enantiomer in PLA polymers. Usually, L-lactic acid is the major constituent with very low amount of D isomer (0.5 – 2 mol%) in high crystalline, fast crystallizing polymers. When the amount of D enantiomer is increased in the range of 4-5 mol%, very slow crystallization rate is observed, whereas in PLA samples with 10 mol% D enantiomer, crystallization is fully suppressed and amorphous materials are obtained.

Although it has been known for a long time, PLA did not find many applications until in mid 80's when copolymers based on PLA with other co-monomers were developed and applied for products such as resorbable sutures and drug-delivery carriers.

In the 90's, increasing pollution originated by non-biodegradable packaging paved the way for the production of PLA packaging such as film, disposable cutlery, cups and dishes. In all these applications, PLA degradability is the property that is exploited thus packaging at the end of life enter the composting stream.

More recently, PLA has attracted also some interest for durable applications such as housing for smartphones, tablets and parts of other electronic equipment. The new P7 server announced by IBM that will be available on the market in 4Q 2014 has four parts of the outer casing moulded with a polymer alloy containing 30 % by weight of PLA.

With all the standard precautions common to all moisture sensitive polyesters, PLA can be processed with many of the standard technologies usually applied to thermoplastic materials. Injection moulding, thermoforming, extrusion casting for films and slabs, blown film and stretch blow moulding for bottles are currently applied.

Precision processing like laser cutting or welding is still in its early development stages, at least for high volume applications. Indeed, laser cutting and sintering has been reported for a few applications in the biomedical sector. Grablow and co-workers cut vascular stents out of PLLA and plasticized PLLA using a CO_2 laser [1]. The reported results showed a dramatic influence of the plasticizer content and sterilization procedure on the mechanical properties of the material. Laser cutting had a lesser effect. Laser radiation has also been used to selective melting or sintering. Li and co-workers prepared porous scaffolds via selective laser sintering of PLA based compounds [2]. Laser radiation has also been applied to melt electro spinning of PLA nano-fibres. Ogata and co-workers prepared nano-fibres by direct melting of pellets or preformed rods, using a CO_2 laser [3-5]. Selective laser melting (SLM) has been applied to make biodegradable bone substitute and it has positively compared with more traditional processing techniques in term of reduced polymer degradation [6].

In these examples, a precise manufacturing process was applied to produce very low volume but high added values products for biomedical applications. Currently PLA films are mainly applied in packaging, for examples pouches for organic vegetables and labelling. At the moment the market volume is still small but many studies and reports forecast a rapid growth for PLA films.

In the mentioned applications sealing is usually done by heat blades or solvents. The aim of the present study is testing the application of laser welding, a highly precise manufacturing technology, to PLA films for the increasing packaging market. A non-contact sealing process by means of a highly efficient laser beam, compared to a sealing process by hot plates, can be advantageous for different reasons [7-9]: a narrow weld seam can be realized without thermal degradation of the material; no mechanical parts in contact means that contamination won't be possible; a speed-up of the process time can be achieved because movements between mechanical parts are avoided and eventually customized tools are not necessary for matching the size and shape of the welding contour line.

2. Materials and their characterization

In the following section, the materials involved in the present experimental work and the adopted methods for their characterization are described.

2.1. Tested materials

A list of the tested materials is shown in the following Tab. 1.

Films were produced in laboratory by means of the compression moulding technique. For this purpose, a 99% pure L-lactic acid polymer (PLA from Sulzer, Switzerland) and, further, two compounds obtained by addition of 10 and 20 % in weight of an impact modifier (PLA_10 and PLA_20, respectively) were used.

The modified PLA was included in this testing plan with the aim to verify its effect on the joining efficiency.

Table 1. List of tested materials.

Material	Tc, T_m (°C)	Crystallinity (%)	Thickness (μm)	Symbol
PLA 99L	116 (broad), 165	25	245 ± 35	PLA
PLA 99L+10 % wt impact modifier (TPU)	-, -	1	150 ± 20	PLA_10
PLA 99L + 20% wt impact modifier (TPU)	115, 168	7	140 ± 15	PLA_20
PLA Commercial	105, 163	16	35 ± 2	PLA_C

Samples of commercial PLA films (PLA_C) were kindly supplied by Sidaplax (Italy). These films can be considered an industrial reference and used for comparison purpose. They were supplied as plain film and also already sealed by heated platen or die for packaging issues.

Thicknesses of tested materials were measured by means of a Palmer's caliper. It is worth noting that the commercial films present a limited deviation compared to the films prepared in the laboratory. It is possible further to observe an effect of the addition of the impact modifier that was an improvement in material formability, in fact, by using the same process parameters, it was possible to produce thinner films.

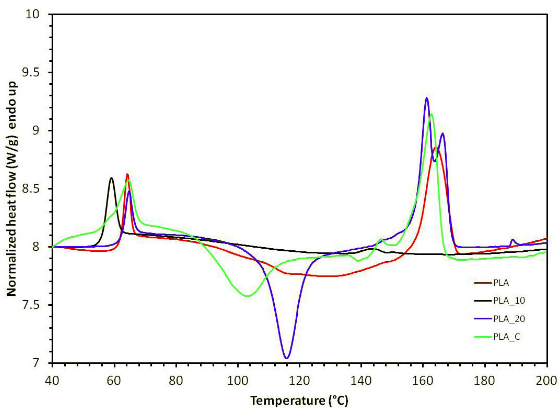

Fig. 1. DSC of considered materials.

2.2. Thermal characterization of polymeric films

A DSC7 (Perkin Elmer) differential scanning calorimeter was used to characterize the thermal properties of the different materials. The thermograms of the different materials are shown in Fig. 1 (the first heating scan is shown in the picture). Measured crystallinity, cold crystallisation (T_c) and melting temperature (T_m) of the considered materials were measured reported in Tab. 1.

2.3. Mechanical characterization of polymeric films

Mechanical characterization of the films has been done by means of an Instrom 5966 testing machine (Fig. 2). Films and welded specimens were cut in order to obtain a simple rectangular shape 20 mm x 120 mm (50 mm was the initial distance between the grips).

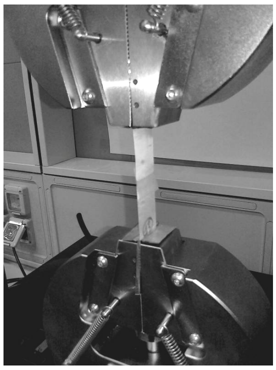

Fig. 2.The mechanical test: a film between the grips of the Instrom 3366.

Testing speed was 3 mm/min in order to achieve a static test.

In Fig. 3 is reported the tensile-elongation curve as obtained for the commercial film and the welded commercial film (PLA_C). The heat-sealing method strongly reduced the plastic behaviour of the material and breakages were observed in the heat-affected zone.

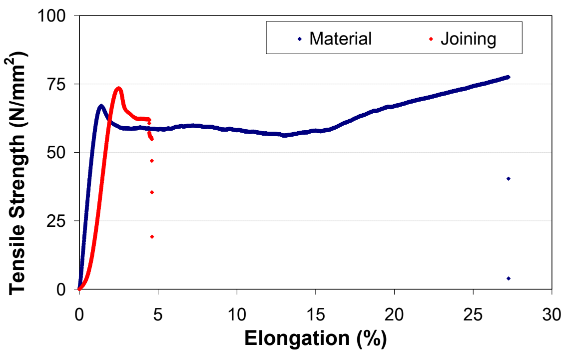

Fig. 3. Curves from the tensile test of the commercial PLA film.

Commercial films show a good replicability of the results, hence only 5 mechanical tests were done for characterizing the film and further 5 more samples were tested for the welded packaging. Some additional comments concerning this point will be written in next paragraph 4.

3. Application of laser-based and solvent-based joining technologies for polymeric films

In the following paragraphs the experimental activity for manufacturing and characterizing the joined films is described.

3.1. Laser welding of PLA films

A 20 W CW Fiber Laser Q-Switched by IPG Photonics was used and focused on the working table by means of a two axis deflection unit by Raylase (Superscan II-10). An aluminium plate made the working table (Fig. 4).

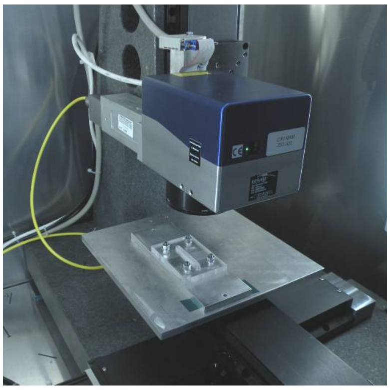

Fig. 4. Laser machining equipment (Superscan II-10 by Raylase).

When joining thin films, a relevant technical aspect must be taken into account: positioning and clamping equipment must realize a good contact between working parts in order to obtain the joining without damaging the films. For this purpose the working table was provided with a number of small holes (diameter 1 mm) and connected to a vacuum pump, which provided the necessary suction force that allowed for holding and fixing the samples.

All the welds were realized in a transmission welding configuration with the maximum available laser power (P = 20 W), a process speed equal to 5.0 mm/s (V), a 200 ns pulse duration (PD) and a 950 kHz pulse frequency (f).

In Fig. 5 is displayed a small portion of a weld as recorded by means of an optical microscope. The molten zone was measured on the top surface and also at the interface between the two films, after destruction of the joint.

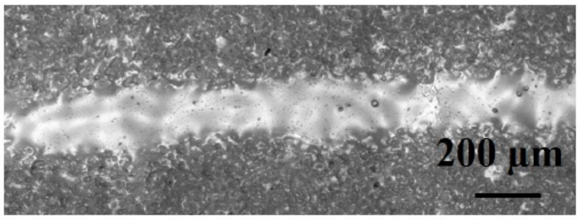

Fig. 5. A small portion of a laser weld in PLA.

The width of the bead depends obviously on the thickness of the joined films and thus, due to the fact that films present different thickness, measured dimensions of the bead resulted dissimilar for different materials. The width of the welds obtained for thicker PLA films were about 250-300 microns; in the case of the thinner impact modified polymeric films the measured widths were about 300-350 micron.

In order to characterize the laser weld 10 samples were prepared for each kind of film.

3.2. Solvent-based technique for joining PLA films

PLA can be easily joined by means of a solvent that allows polymer entanglements. Chloroform, a good solvent for PLA, was used for this purpose. A small amount of chloroform was applied on the film surface using a small paint brush to create the joint and then another film was pressed over for a fixed time. The width of the bead, in this case, was wider than in the case of laser welding and with this technique a 2 mm wide joint was obtained.

In order to characterize the solvent-based joint 10 samples were prepared for each kind of film.

As an example, the tensile test for three samples of an impact modified PLA are reported in Fig. 6: the base material, the laser and the solvent welded sample.

With the aim to compare materials and efficiency of the welding techniques, the data coming from the mechanical characterization were statistically processed and are presented in the following discussion.

4. Discussion for a comparison of the joining efficiencies

10 laser welded or solvent joined samples for

each prepared materials were mechanically tested and compared with the base material.

In the case of the laser joined film, it was possible to observe that all the ruptures occurred in the base material near the weld or in the so-called Heat Affected Zone.

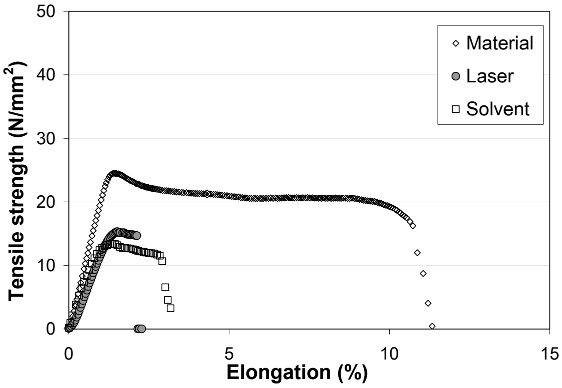

Fig. 6 Tensile strength vs elongation for PLA_10.

In the case of the solvent-based joint, the breakage occurred again near the weld in the Chemical Affected Zone.

In Fig. 7 a comparison between the films produced by compression moulding is summarized in terms of maximum load (yield strength).

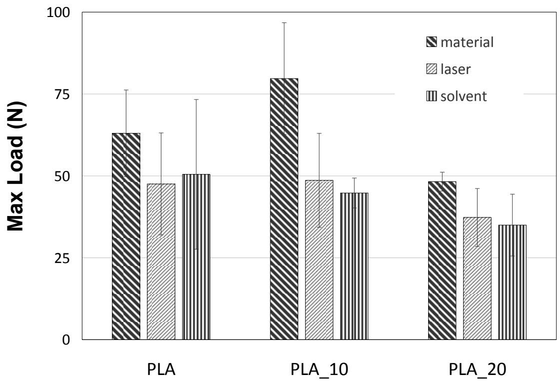

Fig. 7. Comparison amongst maximum load of base material, laser and solvent-based welding.

This diagram has to be revised by introducing the strength due to the fact that different materials have dissimilar thickness.

Tensile strength was obtained dividing the measured load by the area of the transverse section of the films.

In Fig. 8 was introduced also the result obtained for the commercial film.

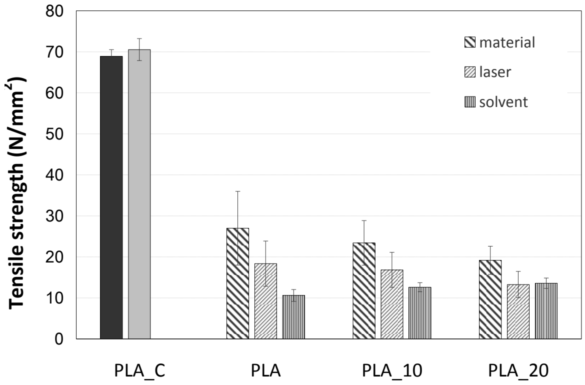

Fig. 8. Comparison between joining efficiency of laser and solvent-based welding.

It is worth noting that: (a) the commercial film shows a tensile strength nearly twice higher than the tensile strength of the compression moulded films; (b) all the compression moulded materials present a wide standard deviation but the effect of the impact modifier was a reduction of the tensile strength; (c) laser welds are more efficient than the solvent-based joints at least if PLA or PLA_10 are considered but (d) an high content in impact modifier reduced the efficiency of the laser welds and in the meantime improved the efficiency of the solvent-based technique.

The higher performances of commercial films (the base material is represented by the black rod and the heat sealed by the grey one in Fig. 8) can be explained by means of a different industrial manufacturing method.

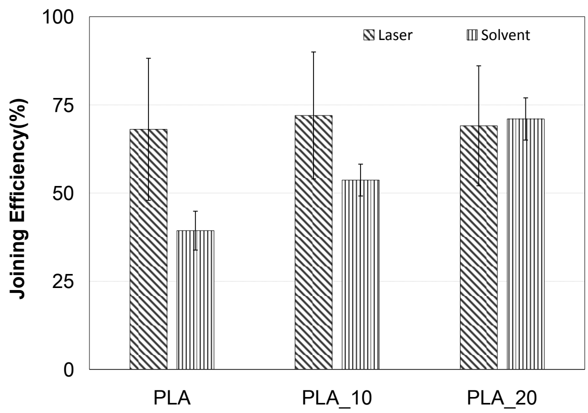

Fig. 9. Comparison amongst tensile strength of base material, laser and solvent-based welding.

The effect of the impact modifier can be better summarized in the following Fig. 9 there the joining efficiency is reported for the considered materials.

The joining efficiency was evaluated by comparison between the tensile strength of the joint and the tensile strength of the base materials equal to 100%.

An additional effect of the solvent was a reduction of the standard deviation.

5. Conclusion

An experimental campaign was planned in order to evaluate weld-ability of PLA by means of two different and concurrent technologies: laser welding and a solvent-based technique. The purpose was the evaluation and the comparison of the joining efficiency. Besides, an impact modifier was used with the aim to increase toughness of PLA with the aim to improve material processability. Two compounds, with 10 and 20 wt% of the impact modifier, were then used for producing films with this purpose.

Further, a commercial PLA film used for packaging, provided by Sidaplax, was tested as an industrial reference.

It is possible to summarize that:

- Laser welding of compression moulded PLA is not dependent on the impact modifier content and the joint efficiency was equal to 75 %.
- Solvent-based joints are sensitive to impact modifier content and an increase in this additive leads to an improvement in tensile performances. The joint efficiency was 40-75.

Acknowledgements

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